

# Study of Crystal Field Parameters for Octahedral Crystal Field

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**Abstract:** The crystal field environment variations give information about many thermodynamic, spectral and magnetic properties. Variation of crystal field affects the inter-electronic repulsion of central ion. In Physics, it forms a very effective tool for calculating the various crystal field parameters in metal complexes. Some complexes of Co(II) metal ion have been synthesized with Glycine as the primary ligand and Pyridine,  $\alpha$ -picoline,  $\beta$ -picoline and oxine as secondary ligand. The FTIR spectra of complexes have been compared with that of free ligand which unveils the coordination of the prime ligand through amino-nitrogen and carboxylic oxygen forming a five membered chelate ring. The electronic spectra of complexes were recorded. The values of different crystal-field parameters  $D_q$ ,  $B$  and  $\beta$  are calculated with the help of Tanabe-Sugano diagram and A. B. P. Lever method.

**Keywords:** Glycine, Crystal-field parameters  $D_q$ , Racah parameter  $B$ , Nephelauxetic Effect  $\beta$ .

## 1. Introduction

Spectral analysis forms a very effective tool for calculating the various crystal-field parameters in transition metal complexes. The excited electronic states help to identify the molecular symmetry, the point group and they allowed us to determine the molecular structure of the metal complexes. The inter-electronic repulsions within a configuration are linear combinations of Coulombic and exchange integrals above the ground term. They are expressed by either of the two ways: Condon -Shortlay parameters

( $F_2$  and  $F_4$ ) and Racah parameters ( $B$  and  $C$ ). The parameter,  $B$  measures the inter-electronic repulsion among the electrons in the d-orbitals in coordination compound complexes. The decrease in the value of the inter-electronic repulsion parameter,  $B$  leads to formation of partial covalent bonding. During the study of the energy level diagram for transition metal ions of  $dn$  configurations, Jorgensen and Schaffer<sup>1-3</sup> observed that the separation between the various  $R-S$  states is not exactly the same in the complex ion as in the free metal ion. The separation between different  $R-S$  states takes place due to the repulsion between the  $d$ -electrons. The decrease in the separation energy between  $d$ -electrons suggests that  $d$ -electron cloud have been expanded in the complex by ligands causing an increase in the mean distance between  $d$ -electron and thus the inter-electronic repulsion is decreased. The different ligands are certainly differently effective in expanding the d-electrons cloud. This effect of ligands in expanding the  $d$ -electron clouds is termed as Nephelauxetic effect. The ratio of the Racah parameter value for metal ion in the complex ( $B$ ) to its value in the free ion ( $B_0$ ) is known as Nephelauxetic effect  $\beta$ . The smaller the value of  $\beta$ , the greater is the covalency between the metal ion and the ligands<sup>4,6</sup>. A number of papers concerning the interpretation of the electronic spectra of transition metal complexes with  $O_h$ -symmetry have been published. In these papers the crystal field parameter  $D_q$  and Racah parameter  $B$  are calculated with allowance for configurational interactions directly from the positions of the bands found in the spectrum<sup>7-10</sup>. The electronic spectra of high-spin octahedral complexes of  $d^7$  configuration shows three spin allowed transitions. The assignment of these transitions with energies associated has been given by A. B. P. Lever for octahedral  $d^7$  complexes<sup>11,12</sup>.

$$(1.1) \quad {}^4T_{2g} \leftarrow {}^4T_{1g}; \nu_1 = 5Dq - 7.5B + \frac{1}{2} [225B^2 + 100Dq^2 + 180DqB]^{1/2},$$

$$(1.2) \quad {}^4A_{2g} \leftarrow {}^4T_{1g}; \nu_2 = 15Dq - 7.5B + \frac{1}{2} [225B^2 + 100Dq^2 + 180DqB]^{1/2},$$

$$(1.3) \quad {}^4T_{2g}(P) \leftarrow {}^4T_{1g}; \nu_3 = [225B^2 + 100Dq^2 + 180DqB]^{1/2},$$

$$(1.4) \quad (\nu_3 - 2\nu_1) = (15B - 10Dq),$$

$$(1.5) \quad (\nu_3 + \nu_2 - 3\nu_1) = 15B.$$

In present paper, we report the calculation of various crystal-field parameters of Co(II) metal-ion octahedral complexes with the help of FTIR and electronic spectra using Tanabe- Sugano diagram and *A. B. P. Lever* method.

2. Experimental Details

For the present study Glycine has been selected as primary ligand and Pyridine,  $\alpha$  -picoline,  $\beta$  -picoline and oxine have been taken as secondary ligands. The ligand have been used for complexation with Co(II) metal-ion by usual method of reflux<sup>13,14</sup>. The *C*, *H* & *N* in the ligand as well as in complexes have been determined by using Elemental Analyser ( CHNS Analyser) of Dept. of Chemistry, IIT Patna. Cobalt content of complexes was determined gravimetrically. Molar conductivity of complex compounds has been determined on Elico Direct Reading Conductivity meter using DMSO solution of  $10^{-3}M$  concentration. The FTIR of ligand and complexes were recorded on Perkin Elmer spectrum version 10.03.05 using Nujolmull. The magnetic susceptibility of complexes was determined on Gouy’s Balance at room temperature using Hg(II) tetrathiocyanato Cobaltate(II) as calibrant. The electronic spectra of complexes were recorded on Lambda 950-Perkin Elmer-UK Spectrophotometer of ACCN, Aryabhatta Knowledge University Patna.

3. Results and Discussion

**3.1 Physical properties:** The physical data and micro analytical data of ligand along with of complexes have been displayed in Table-1. On the basis of these data, the general formula of complexes is found to be  $[CoL_2X_2]$  where *L* = Glycine and *X* = Pyridine,  $\alpha$  -picoline,  $\beta$  -picoline and oxine.

**Table 1.** Consolidated account of colour, melting point, % composition Found/(calculated), molar conductivity and magnetic moment of Co(II) metal complexes

| Comple<br>x | Colour | Melti<br>ng<br>Point<br>( in<br>°C) | Metal<br>(%)<br><div>found<br/>(calculated)</div> | Carbo<br>n (%)<br><div>found<br/>(calculated)</div> | Hydrog<br>en<br>(%)<br><div>found<br/>(calculated)</div> | Nitro<br>gen<br>(%)<br><div>found<br/>(calculated)</div> | Molar<br>Conducti<br>vity<br>( $\lambda_m$ )<br>( $Ohm^{-1}$<br>$cm^2$ ) | Magne<br>tic<br>mome<br>nt<br>( $\mu_{eff}$ in |
|-------------|--------|-------------------------------------|---------------------------------------------------|-----------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------|--------------------------------------------------------------------------|------------------------------------------------|
|-------------|--------|-------------------------------------|---------------------------------------------------|-----------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------|--------------------------------------------------------------------------|------------------------------------------------|

|                                                        |                         |       |                  |                  |                |                  | mol <sup>-1</sup> ) | B.M.) |
|--------------------------------------------------------|-------------------------|-------|------------------|------------------|----------------|------------------|---------------------|-------|
| Ligand<br>(Glycine)<br>$\alpha$ -aminoacetic acid      | Yellow<br>(pearl white) | 232.5 | -----            | 32.89<br>(32)    | 6.42<br>(6.67) | 18.35<br>(18.67) | -----               | ----- |
| [Co(Gly) <sub>2</sub> (Py) <sub>2</sub> ]              | Light Pink              | 248   | 15.75<br>(15.93) | 46.32<br>(46.15) | 4.80<br>(4.94) | 15.16<br>(15.38) | 14.00               | 4.93  |
| [Co(Gly) <sub>2</sub> ( $\alpha$ -pico) <sub>2</sub> ] | Bright Pink             | 293   | 14.58<br>(14.79) | 49.15<br>(48.37) | 5.42<br>(5.61) | 14.11<br>(14.28) | 14.00               | 4.93  |
| [Co(Gly) <sub>2</sub> ( $\beta$ -pico) <sub>2</sub> ]  | Pinkish Red             | 298   | 14.61<br>(14.79) | 49.20<br>(48.97) | 5.38<br>(5.61) | 14.00<br>(14.28) | 13.00               | 4.93  |
| [Co(Gly) <sub>2</sub> (oxine) <sub>2</sub> ]           | Dull Pink               | 272   | 11.53<br>(11.69) | 53.10<br>(53.22) | 4.26<br>(4.43) | 11.16<br>(11.29) | 13.50               | 4.92  |

**3.2 FTIR spectra:** The mode of coordination of the ligand to the metal ions has been ascertained by the comparison of FTIR- spectra of the complexes with that of the free ligand. The important diagnostic bands in the infra-red spectra of free ligand were assigned and the graphical presentation has been given in Fig.1.

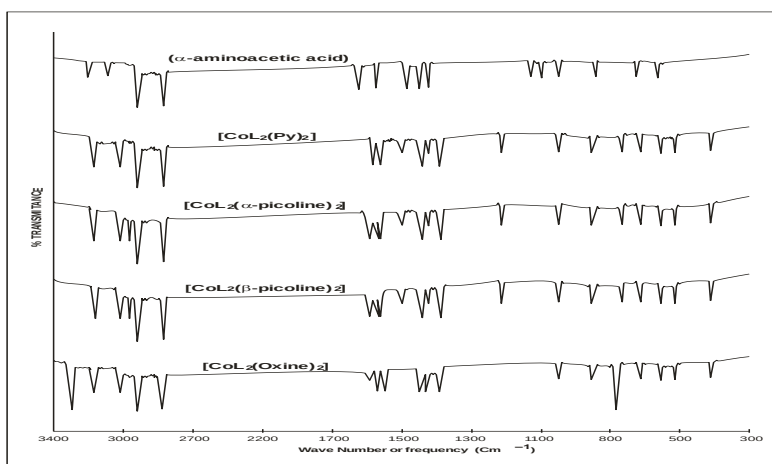


**Figure 1.** Comparative graphical presentation of FTIR- spectra of the complexes with that of the free ligand

For clarity the comparison of the FTIR-bands of complexes with that of free ligand has been presented in Table-2.

**Table 2.** Important FTIR bands with assignment ( $\text{cm}^{-1}$ )

| Complex                                                | $\nu_{\text{asym}} \text{NH}_2$<br>( $\text{cm}^{-1}$ ) | $\nu_{\text{sym}} \text{NH}_2$<br>( $\text{cm}^{-1}$ ) | $\nu_{\text{asym}} \text{COO}^-$<br>( $\text{cm}^{-1}$ ) | $\nu_{\text{sym}} \text{COO}^-$<br>( $\text{cm}^{-1}$ ) | $\nu_{\text{M-N}}$<br>( $\text{cm}^{-1}$ ) | $\nu_{\text{M-O}}$<br>( $\text{cm}^{-1}$ ) | New Bands<br>( $\text{cm}^{-1}$ ) | Assignment of new bands                        |
|--------------------------------------------------------|---------------------------------------------------------|--------------------------------------------------------|----------------------------------------------------------|---------------------------------------------------------|--------------------------------------------|--------------------------------------------|-----------------------------------|------------------------------------------------|
| Ligand<br>(Glycine)<br>$\alpha$ -aminoacetic acid      | 3200                                                    | 3075                                                   | 1620                                                     | 1425                                                    | -----                                      | -----<br>-                                 | -----                             | -----                                          |
| [Co(Gly) <sub>2</sub> (Py) <sub>2</sub> ]              | 3170                                                    | 3032                                                   | 1570                                                     | 1400                                                    | 510                                        | 410                                        | 1590<br>1570<br>1500<br>1430      | Breathing vibration of pyridine ring           |
| [Co(Gly) <sub>2</sub> ( $\alpha$ -pico) <sub>2</sub> ] | 3175                                                    | 3030                                                   | 1575                                                     | 1400                                                    | 505                                        | 415                                        | 1595<br>1565<br>1500<br>1420      | Breathing vibration of $\alpha$ -picoline ring |
| [Co(Gly) <sub>2</sub> ( $\beta$ -pico) <sub>2</sub> ]  | 3172                                                    | 3030                                                   | 1575                                                     | 1400                                                    | 505                                        | 415                                        | 1595<br>1565<br>1500<br>1420      | Breathing vibration of $\beta$ -picoline ring  |
| [Co(Gly) <sub>2</sub> (oxine) <sub>2</sub> ]           | 3174                                                    | 3030                                                   | 1575                                                     | 1400                                                    | 505                                        | 415                                        | 1585<br>1560<br>1465              | Breathing vibration of oxine ring              |

The free ligand absorbs at  $3200 \text{ cm}^{-1}$  &  $3075 \text{ cm}^{-1}$  with weak intensity due to  $\nu_{\text{asym}} \text{NH}_2$  and  $\nu_{\text{sym}} \text{NH}_2$  stretching vibrations respectively<sup>15-18</sup>. The medium band appearing at  $1580 \text{ cm}^{-1}$  and  $1490 \text{ cm}^{-1}$  has fairly will assigned to  $\delta_{\text{asym}} \text{NH}_3^+$  and  $\delta_{\text{sym}} \text{NH}_3^+$ <sup>19,20</sup>. It makes it clear that Glycine exists in zwitter ionic form i.e.  $\text{NH}_3^+ - \text{CH}_2 - \text{COO}^-$ . These deformational vibrational bands disappear in the spectra of complexes. The band appearing at  $3200 \text{ cm}^{-1}$  and

3075  $\text{cm}^{-1}$  due to  $\nu_{\text{asym}} \text{NH}_2$  and  $\nu_{\text{sym}} \text{NH}_2$  of free ligand are found to have undergone changes in the FTIR spectra of complexes wherein they appear at 3170  $\text{cm}^{-1}$  to 3175  $\text{cm}^{-1}$  and 3030  $\text{cm}^{-1}$  with medium intensity. It clearly indicates that nitrogen of  $\text{NH}_2$  group is involved in co-ordination to the metal-ion in complexes<sup>21,22</sup>. The other major change is found in the vibrational absorption  $\text{COO}^-$  which changes from 1620  $\text{cm}^{-1}$  and 1425  $\text{cm}^{-1}$  due to  $\nu_{\text{asym}} \text{COO}^-$  and  $\nu_{\text{sym}} \text{COO}^-$  to 1570  $\text{cm}^{-1}$  – 1580  $\text{cm}^{-1}$  and 1390  $\text{cm}^{-1}$  – 1400  $\text{cm}^{-1}$  in FTIR-spectra of complexes. It shows that during complexation the deprotonation of the ligand has taken place followed by its coordination through oxygen<sup>23, 24</sup>. The separation between  $\nu_{\text{asym}} \text{COO}^-$  and  $\nu_{\text{sym}} \text{COO}^-$  of 180  $\text{cm}^{-1}$  shows that monodenticity of  $\text{COO}^-$  group<sup>25</sup>. Our supposition of the ligand through amino group nitrogen and carboxylic group oxygen is further confirmed by new bands appearing at 500  $\text{cm}^{-1}$  – 510  $\text{cm}^{-1}$  and 420  $\text{cm}^{-1}$  – 480  $\text{cm}^{-1}$  due to  $\nu_{\text{M-N}}$  and  $\nu_{\text{M-O}}$  stretching vibration respectively<sup>26</sup>. The appearance of new bands between 1600  $\text{cm}^{-1}$  – 1400  $\text{cm}^{-1}$  and 700  $\text{cm}^{-1}$  – 1200  $\text{cm}^{-1}$  predict the presence of pyridine, picoline and oxine within the coordination sphere of these complexes<sup>27-29</sup>.

**3.3 Magnetic moment and Electronic spectra:** Magnetic moment of Co(II) complexes has been found 4.92 – 4.93 BM. The  $\mu_s$  and  $\mu_{s+L}$  value of Co(II) complexes should be 3.87 BM and 5.20 BM. The value is less than 5.20 BM due to spin-orbit coupling which further restrict the spin as well as orbital motion of the electron to the little extent. The magnetic moment values however are in good agreement with the values for octahedral complexes of Co(II)<sup>30, 31</sup>. The electronic spectra of Co(II) complexes is very interesting and have extensively been studied as the spectra are indicative of their stereochemistry. The electronic spectra of Co(II) complexes is represented in Figure-2.

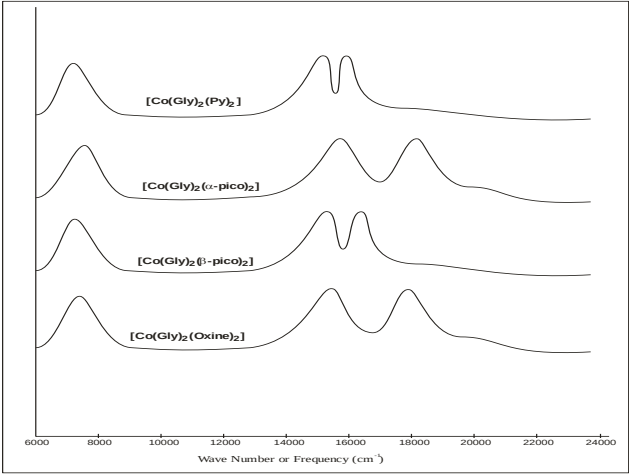


Figure 2. UV-Vis spectra of Co(II) Complexes

Co(II) is a  $d^7$  system for which the ground state term is  $^4F$  and the next excited state with the same spin multiplicity is  $^4P$ . Under the perturbation of octahedral crystal field  $^4P$  term doesn't split and it only gets transformed into  $^4T_{1g}$  (P) but  $^4F$  undergoes splitting as in Figure-3.

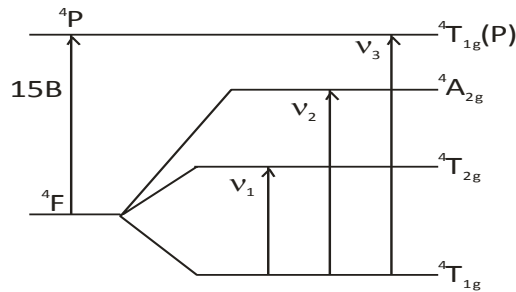


Figure 3. Transitions of Co(II) Complexes

The position of electronic spectral band has been given in Table-3.

Table 3. Electronic spectral bands of Co(II) metal complexes

| Complex                                               | $\nu_1$ (in $\text{cm}^{-1}$ ) | $\nu_2$ (in $\text{cm}^{-1}$ ) | $\nu_3$ (in $\text{cm}^{-1}$ ) |
|-------------------------------------------------------|--------------------------------|--------------------------------|--------------------------------|
| $[\text{Co}(\text{Gly})_2(\text{Py})_2]$              | 7150                           | 15230                          | 15945                          |
| $[\text{Co}(\text{Gly})_2(\alpha\text{-picoline})_2]$ | 7300                           | 15625                          | 18145                          |
| $[\text{Co}(\text{Gly})_2(\beta\text{-picoline})_2]$  | 7200                           | 15360                          | 16420                          |
| $[\text{Co}(\text{Gly})_2(\text{oxine})_2]$           | 7230                           | 15480                          | 17970                          |

**3.4 Calculation of different crystal-field parameters:** (a) The data obtained were used to calculate the values of different crystal-field



So, reduction in the Racah parameter after complexation =  $971 - 810 = 161 \text{ cm}^{-1}$ . Hence, Nephelauxetic Effect  $\beta = \frac{B}{B_0} = \frac{810}{971} = 0.834$ .

Similarly we have calculated these crystal field parameters for other Co(II) metal complexes and its values are summarised in Table-4.

**Table 4.** Values of different crystal field parameters of Co(II) complexes

| Complex                                                    | $\nu_2 / \nu_1$ | $\nu_3 / \nu_1$ | $\nu_3 / \nu_2$ | $10D_q$<br>(in $\text{cm}^{-1}$ ) | $B$<br>(in $\text{cm}^{-1}$ ) | Reduction<br>in $B$ (in $\text{cm}^{-1}$ ) | $\beta$ |
|------------------------------------------------------------|-----------------|-----------------|-----------------|-----------------------------------|-------------------------------|--------------------------------------------|---------|
| [Co(Gly) <sub>2</sub> (Py) <sub>2</sub> ]                  | 2.130           | 2.230           | 1.046           | 8100                              | 647.9                         | 161                                        | 0.834   |
| [Co(Gly) <sub>2</sub> ( $\alpha$ -picoline) <sub>2</sub> ] | 2.140           | 2.486           | 1.160           | 8560                              | 778.0                         | 193                                        | 0.801   |
| [Co(Gly) <sub>2</sub> ( $\beta$ -picoline) <sub>2</sub> ]  | 2.133           | 2.280           | 1.069           | 8500                              | 708.4                         | 262.6                                      | 0.729   |
| [Co(Gly) <sub>2</sub> (oxi ne) <sub>2</sub> ]              | 2.140           | 2.485           | 1.160           | 8230                              | 799                           | 172                                        | 0.823   |

(b) Using *A. B. P. Lever Method*,  $D_q$  and  $B$  have been calculated. The Nephelauxetic effect  $\beta$  has also been calculated as  $\beta = B/B_0$ .

**For [Co(Gly)<sub>2</sub>(Py)<sub>2</sub>]:**  ${}^4T_{2g} \leftarrow {}^4T_{1g}$ ;  $\nu_1 = 7150 \text{ cm}^{-1}$ ,

${}^4A_{2g} \leftarrow {}^4T_{1g}$ ;  $\nu_2 = 15230 \text{ cm}^{-1}$ ,  ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}$ ;  $\nu_3 = 15945 \text{ cm}^{-1}$ ,

As  $(\nu_3 + \nu_2 - 3\nu_1) = 15B \Rightarrow B = 648.33 \text{ cm}^{-1}$

(i) As  $\nu_1 = \left[ 5D_q - \frac{15}{2}B + \frac{1}{2}\sqrt{225B^2 + 100D_q^2 + 180D_qB} \right]$ , hence

$$7150 = [5D_q - (7.5 \times 648.33) + \frac{1}{2}\sqrt{225 \times (648.33)^2 + 100D_q^2 + (180 \times 648.33)D_q}]$$

$$\Rightarrow D_q = 808.0706 \text{ cm}^{-1}$$

(ii) As  $\nu_3 = \sqrt{225B^2 + 100D_q^2 + 180D_qB}$ , hence

$$15945 = \sqrt{225 \times (648.33)^2 + 100D_q^2 + (180 \times 648.33)D_q} \Rightarrow D_q = 808.319 \text{ cm}^{-1}$$

(iii) As  $\nu_3 = \sqrt{225B^2 + 100D_q^2 + 180D_qB}$ , hence

$$15945 = \sqrt{225 \times (648.33)^2 + 100D_q^2 + (180 \times 648.33)D_q} \Rightarrow D_q = 808.319 \text{ cm}^{-1}$$

Hence, average of  $D_q = \frac{808.146 + 808.071 + 808.319}{3} = \frac{242.536}{3}$

$$= 808.17866 \approx 808.179 \text{ cm}^{-1} \Rightarrow D_q = 808.179 \text{ cm}^{-1} \therefore 10 D_q = 8081.79 \text{ cm}^{-1}$$

$$\Rightarrow (\text{Reduction in } B) = B_o - B = 971 - 648.33 = 322.67 \text{ cm}^{-1} \quad \text{and,}$$

$$\text{Nephelauxetic effect } \beta = \frac{B}{B_o} = \frac{648.33}{971} = 0.667,$$

Similarly we have calculated these crystal field parameters for other Co(II) complexes and its values are displayed in Table-5.

**Table 5.** Values of different crystal field parameters of Co(II) metal complexes

| Complex                                                    | $D_q$<br>(in $\text{cm}^{-1}$ ) | $10D_q$<br>(in $\text{cm}^{-1}$ ) | $B$<br>(in $\text{cm}^{-1}$ ) | Reduction<br>in $B = (B_o - B)$<br>(in $\text{cm}^{-1}$ ) | $\beta$ |
|------------------------------------------------------------|---------------------------------|-----------------------------------|-------------------------------|-----------------------------------------------------------|---------|
| [Co(Gly) <sub>2</sub> (Py) <sub>2</sub> ]                  | 808.179                         | 8081.79                           | 648.33                        | 322.67                                                    | 0.667   |
| [Co(Gly) <sub>2</sub> ( $\alpha$ -picoline) <sub>2</sub> ] | 833.331                         | 8333.31                           | 791.33                        | 179.67                                                    | 0.814   |
| [Co(Gly) <sub>2</sub> ( $\beta$ -picoline) <sub>2</sub> ]  | 815.442                         | 8154.42                           | 678.66                        | 292.34                                                    | 0.699   |
| [Co(Gly) <sub>2</sub> (oxine) <sub>2</sub> ]               | 825.250                         | 8252.50                           | 784                           | 187.00                                                    | 0.807   |

We can see that these values of crystal-field parameters are in good agreement with the reported values for Co(II) octahedral complexes<sup>32, 33</sup>.

#### 4. Conclusion

There is no appreciable deviation of the values of  $D_q$ ,  $B$  and  $\beta$  calculated from Tanabe – Sugano diagram and A. B. P. Lever method for Co(II) metal complexes with  $O_h$  - symmetry. The study shows that in all the complexes the Racah parameter ( $B$ ) has decreased in respect of free Co(II)-ion ( $B_o = 971 \text{ cm}^{-1}$ ). It is strong evidence that the electron cloud density have undergone spreading from metal ion to the ligand orbitals.

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